

**DEVELOPMENT OF BIMETALLIC CATALYST Ni-Co/MgO-ZrO₂ FOR
REFORMING OF METHANE USING CARBON DIOXIDE**

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UNIVERSITI SAINS MALAYSIA

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REFORMING OF METHANE USING CARBON DIOXIDE**

by

FAN MUN SING

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LIST OF ABBREVIATIONS

Symbol	Description
AAS	Atomic Absorption Spectroscopy
AMREC	Advanced Material Research Centre
BET	Brunauer–Emmett–Teller
BJH	Barret-Joyner-Halenda
CCD	Centred Composite Design
CDRM	Carbon dioxide reforming
CETS	chemical energy transmission system
CMZ	Co/MgO-ZrO ₂
DOE	Design of Experiments
DTA	Differential Thermal Analysis
EPR	Electron Paramagnetic Resonance
FTIR	Fourier Transform Infrared
GHSV	gas hourly space velocity
GTL	Gas-to-Liquid
HRTEM	High resolution transmission electron microscope
IPA/LN ₂	Isopropyl Alcohol-Liquid Nitrogen
MS	Mass Spectrometry
NMZ	Ni/MgO-ZrO ₂
NCMZ	Ni-Co/MgO-ZrO ₂
OD	Outer Diameter
POM	Partial oxidation of methane
RDS	Rate Determining Step
RSM	Response Surface Methodology
RWGS	Reversed water gas shift
SAED	Selected area electron diffraction
SEM	Scanning Electron Microscope
SMSIs	strong metal–support interactions
SRM	Steam reforming of methane
TCD	Thermo conductivity detector
TG	Thermogravimetric
TPH	Temperature Programmed Hydrogenation

TPR	Temperature Programmed Reduction
TPSR	Temperature Programmed Surface Reaction
TPO	Temperature Programmed Oxidation
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

LIST OF SYMBOL

Symbol	Description	Unit
-	Low level	-
+	High level	-
P_i	Partial pressure of component i	kPa
K_1	Equilibrium constant	kPa
k_2	Equilibrium constant	mol/g/s
K_3	Equilibrium constant	kPa
k_4	Equilibrium constant	mol/g/s
r	Rate of reaction	mol/g/s
Greek letters		
α	Distance of the axial point from center in DOE	-
β_o	Offset term in DOE model	-
β_i	Linear term in DOE model	-
β_{ii}	Quadratic term in DOE model	-
β_{ij}	Interaction term in DOE model	-
ε	error	-

**PEMBANGUNAN MANGKIN DWILOGAM Ni-Co/MgO-ZrO₂ UNTUK
PEMBENTUKAN SEMULA METANA MENGGUNAKAN KARBON
DIOKSIDA**

ABSTRAK

Pembentukan semula metana dengan karbon dioksida (CDRM) adalah kaedah yang berpotensi untuk memanfaatkan gas rumah kaca (CO₂ dan CH₄) untuk menghasilkan gas sintesis sebagai bahan suapan untuk pengeluaran bahan bakar cecair melalui proses Fischer-Tropsch.

Mangkin nikel (6 peratusan berat), kobalt (6 peratusan berat) dan Ni-Co (3 peratusan berat Ni dan 3 peratusan berat Co) disokong pada mesopori MgO-ZrO₂ berliang meso disediakan menggunakan kaedah impregnasi berbantuan surfaktan. Proses CDRM menggunakan mangkin tersebut dikaji di dalam reaktor balang kuarza pada 750 °C, 1 atm dengan halaju ruang gas per jam pada 125000 mL/g/jam. Berdasarkan penukaran bahan tindakbalas dan hasil gas sintesis dalam aliran produk, mangkin dwilogam Ni-Co/MgO-ZrO₂ (NCMZ) didapati paling sesuai untuk process ini. Ia menunjukkan aktiviti yang tinggi dan stabil selama 40 jam dengan penukaran metana dan karbon dioksida sebanyak 80% dan 84%, masing-masing. Nisbah syngas yang didapati adalah hampir satu, tanpa penyahaktifan yang nyata berbanding dengan mangkin monologam masing-masing. Mangkin ini juga boleh dipulihkan semula dengan baik dan memperoleh semula aktiviti mangkin awal melalui pemulihan semula dalam udara selama 1 jam. Prestasi mangkin yang tinggi adalah disebabkan oleh penyerakan logam yang seragam, zarah logam yang kecil dan kesan sinergi di antara Ni dan Co. Mangkin dwilogam tersebut memiliki kemampuan untuk

menghalang pengoksidaan logam dan menunjukkan kewujudan spesies oksigen permukaan yang lebih tinggi yang bertanggungjawab kestabilannya.

Kinetik untuk proses CDRM menggunakan mangkin dwilogam NCMZ diselidiki dalam reaktor tetap pada julat suhu 650-750 °C dan tekanan separa CO₂ dan CH₄ antara 45-360 kPa. Disebabkan tindakbalas serentak pembentukan semula CO₂ dan anjakan berbalik gas air (RWGS), tenaga pengaktifan ketara berbeza daripada yang dilaporkan iaitu sebanyak 52.9 dan 48.1 kJ/mol untuk penggunaan CH₄ dan CO₂, masing-masing. Model Langmuir-Hinshelwood (LHHW) dicadangkan berdasarkan kepada pemisahan CH₄ sebagai langkah penentu kadar dan didapati sepadan dengan data eksperimen.

Rekabentuk Eksperimen (DOE) telah digunakan untuk mengkaji hubungan antara nisbah karbon dioksida kepada metana (1-5), kelajuan gas per jam (8400-200000 mL/g/h), kepekatan oksigen dalam suapan (3 -8%) dan suhu tindakbalas (700-800 °C). Berdasarkan ANOVA, model setiap gerakbalas yang berkaitan dengan pembolehubah adalah signifikan dan boleh digunakan untuk mengoptimumkan proses melalui kaedah sambutan permukaan. Keadaan optimum proses diperolehi pada GHSV 145190 mL/g/h, suhu 749 °C, nisbah karbon dioksida kepada metana ialah 3 dan 7% penambahan oksigen dalam suapan. Ulangan tindakbalas pada keadaan optimum memberikan respon yang sesuai dengan model jawapan yang disimulasikan dengan ralat $\pm 2\%$.

DEVELOPMENT OF BIMETALLIC CATALYST Ni-Co/MgO-ZrO₂ FOR REFORMING OF METHANE USING CARBON DIOXIDE

ABSTRACT

Carbon dioxide reforming of methane (CDRM) is a potential method to utilize the greenhouse gases (CO₂ and CH₄) to produce syngas as the feedstock for the production of liquid fuel through Fischer-Tropsch process.

Nickel (6 wt% Ni), cobalt (6 wt% Co) and Ni-Co (3 wt% Ni and 3 wt% Co) supported over mesoporous MgO-ZrO₂ as catalysts were prepared using a surfactant assisted-impregnation method. CDRM process using these catalysts were studied in a quartz tube microreactor at 750 °C, 1 atm with gas hourly space velocity of 125,000 mL/g/h. Based on reactant's conversion and syngas yield in the product stream, bimetallic catalyst Ni-Co/MgO-ZrO₂ (NCMZ) was a suitable catalyst for carbon dioxide reforming. The bimetallic catalyst exhibited high and stable activity during 40 h reaction time with methane and carbon dioxide conversions of 80 % and 84 %, respectively. The syngas ratio was close to unity, without significant deactivation as compared to the respective monometallic catalysts. The bimetallic catalyst also exhibited excellent regenerability by restoring its initial catalytic activity through 1 h of regeneration treatment in air. The high performance of the catalyst was due to better metal dispersion, small metal particle size and synergetic effect between Ni and Co particles. The XPS results showed that bimetallic catalyst had the ability to hinder metal oxidation and exhibited the presence of higher surface oxygen species which was responsible to maintain the stability of the catalyst.

Kinetics of CDRM process over NCMZ bimetallic catalyst was investigated in a fixed bed reactor at a temperature range of 650–750 °C and the partial pressures of CO₂ and CH₄ ranged from 45 to 360 kPa. Owing to simultaneous occurrence of CO₂ reforming reaction and reverse water–gas shift reaction (RWGS) in the system, the apparent activation energies were found to be different from those reported and they were 52.9 and 48.1 kJ/mol for CH₄ and CO₂ consumption, respectively. A Langmuir–Hinshelwood (LHHW) model was proposed based on the dissociation of CH₄ as the rate determining step over the NCMZ catalyst. It satisfactorily fits the experimental data as well.

Design of Experiments (DOE) were used to study the relationship between the process variables such as carbon dioxide to methane ratios (1-5), gas hourly space velocity (8400-200000 mL/g/h), oxygen concentration in feed (3-8 %) and reaction temperature (700-800 °C). Methane conversion, hydrogen and carbon monoxide yields, and syngas ratio were considered as the responses to study the effect of process variables using ANOVA analysis embedded in Design Expert software. The ANOVA results indicated that the model of each response related with the process variable effects was significant and could be used to optimize the reforming process through response surface methodology. The optimum reaction condition for carbon dioxide reforming was obtained as gas hourly space velocity (GHSV) of 145190 mL/g/h, reaction temperature of 749 °C, carbon dioxide to methane ratio of 3 and 7 % of oxygen addition in the feed. The repeated experiments conducted at the optimum condition gave the responses which were in agreement with the simulated model responses within an error of ± 2 %.

CHAPTER 1

INTRODUCTION

This chapter gives an overview to the background and the development of synthesis gas (syngas) production technology through various reforming processes. The current trend in syngas through carbon dioxide reforming of methane is discussed. This chapter also concludes with the problem statement, research objectives, scope and the structure of the thesis.

1.1 Natural Gas Utilization

Fossil fuels have become an important part of everyday life, providing us with a multitude of materials, energy and fuels. In the twentieth century, oil played the most important role. Its relatively recent first commercial extraction in 1859 allowed a number of important developments, starting with cheap illumination fuel (to replace expensive sperm whale spermaceti), then the road usage vehicles, and on to powered flight and commercial air travel (Jones Roger, 2006). As a result, oil has become the driving force for the world's economy, providing the raw materials for >90 % of the organic chemicals produced in 1980 and has become the dominant source of transportation fuels (Jones Roger, 2006, Maity *et al.*, 2010, Murphy and Oliveira, 2010, Nashawi *et al.*, 2010). However, the finite and readily accessible oil reserves are being quickly depleted and with the fast development of the Asian economies this process can be advanced (Nashawi *et al.*, 2010, Pibasso, 2010, Snow, 2010). In recent years, the oil price has again rocketed, reaching an all time high of around \$ 80 per barrel (Chen *et al.*, 2010, Hedi Arouri and Khuong Nguyen, 2010, Radler, 2010), again focusing the world's attention on the importance of oil. Therefore, alternative energy resources are required.

One alternative is natural gas, which is composed predominantly of methane, and is forecast to outlast oil by a significant margin (Bybee, 2010, Lee and Sidle, 2010, Pibasso, 2010). Increasing exploration has led to a shift in the location of known reserves in more remote regions, away from the areas of consumption and into less hospitable areas which results in increasing transportation costs and the need to convert natural gas into more economically attractive products, such as liquid transportation fuels of higher energy density (York *et al.*, 2007). Therefore, there has been considerable investment in research programs, both academic and industrial, for the development of routes from methane to liquid synfuels as substitutes to petroleum.

Hydrocarbon upgrading of natural gas has been a challenge for the industries as well as researchers throughout the world (Ashcroft *et al.*, 1990, Lin and Sen, 1994, Periana *et al.*, 1998, Choudhary *et al.*, 2005, Hao *et al.*, 2008, Cho *et al.*, 2010). Methane (CH_4), can be chemically converted into higher hydrocarbons as well as liquid fuels chemically through indirect and direct routes (Choudhary *et al.*, 2003). The direct routes (oxidative coupling of methane (OCM) (Greish *et al.*, 2009, Kundu *et al.*, 2009, Fallah and Falamaki, 2010, Gholipour *et al.*, 2010), and methane aromatization (Luzgin *et al.*, 2009, Masiero *et al.*, 2009) are single-step processes in which the methane is chemically reacted with oxygen (or another oxidizing species) to give the desired product directly. Apart from complete combustion for heating purposes (giving CO_2 and water), all other possible processes are still at under the development stage.

Direct methane upgrading routes are not commercially applicable. This is mostly due to unfavourable thermodynamic conditions that cause low conversions and selectivities and thus not economically viable (Choudhary *et al.*, 2003, York *et al.*, 2003). Meanwhile, the indirect routes which draw the most attention recently in this area of research are focused on the methane upgrading via synthesis gas (syngas), which is a mixture of hydrogen and carbon monoxide formed from the reaction of methane with oxygen, steam, carbon dioxide and combination among these components.

Gas-to-Liquid (GTL) technology is the most widely accepted technologies that convert natural gas into clean diesel, naphtha, kerosene and light oils, and these products can be distributed through the same channels as other petroleum products. GTL process involves conversion of methane into syngas in the first step followed by conversion of syngas to higher hydrocarbon or liquid fuels in the second step by the Fischer-Tropsch process (Arzamendi *et al.*, 2010, Derevich, 2010, James *et al.*, 2010). The utilization of natural gas through syngas is presented in Figure 1.1.

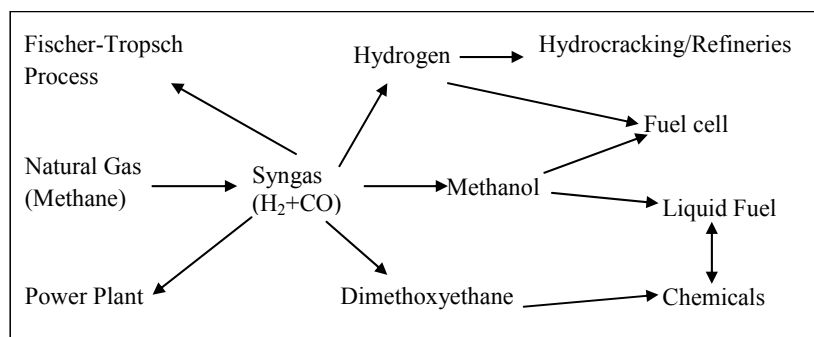


Figure 1.1: Indirect routes for natural gas upgrading through syngas (Choudhary and Choudhary, 2008)

Figure 1.1 shows that a large number of useful chemicals can be obtained from syngas which is one of the most important chemical industries feedstocks. However, the generation of syngas from methane is a large capital investment. Perhaps, it is the major investment part in the indirect methane conversion processes (Bakkerud *et al.*, 2004). As a result, wide-ranging studies are being undertaken in academia as well as in industry to develop energy-efficient processes for syngas generation.

1.2 Syngas Utilization

Felice Fontana, an Italian physicist who first synthesized “blue water gas” (syngas) in 1780 by passing steam over red hot coal (Platon and Wang, 2002). Since then various routes have been suggested for the conversion of syngas to transportation fuels. These routes can be divided as follows, with the emphasis on potential industrial applications (York *et al.*, 2007):

1. Fischer-Tropsch synthesis;
2. Methanol; and
3. Methanol to gasoline (MTG) and distillates (MOGD).

1.3 Reforming Technologies for Syngas Production

Steam reforming of methane, partial oxidation of methane reforming, and carbon dioxide reforming of methane (dry reforming), are the three major processes for the production of syngas as presented in Table 1.1.

Table 1.1: Reforming processes for syngas production (Choudhary and Choudhary, 2008)

Reforming Process	Process Equation	Syngas Ratio(H ₂ /CO)	ΔH _{298k} (kJ/mol)
Steam Reforming	CH ₄ +H ₂ O→CO+3H ₂	3	206
CO ₂ Reforming	CH ₄ +CO ₂ →2CO+2H ₂	1	247
Partial Oxidation	CH ₄ +(1/2)O ₂ →CO+2H ₂	2	-35.5

1.3.1 Steam Reforming

Steam reforming process, was first commercialized in 1930s, and is currently the most widely used process for methane conversion (Rostrup-Nielsen, 1993). Steam reforming of methane (SRM) is an endothermic reaction and is carried out with excess steam to produce H₂ and CO in the presence of catalyst (Dicks *et al.*, 2000, Ma *et al.*, 2008, Arzamendi *et al.*, 2009, Nikolla *et al.*, 2009). The steam reforming process is highly endothermic (energy intensive) and produces 3 mol of hydrogen per mole of methane consumed. If hydrogen production is the goal (e.g. at refineries and hydrocracking), the amount of hydrogen produced can be further increased by utilizing the water gas shift reaction, wherein carbon monoxide is reacted with steam to produce carbon dioxide and hydrogen (Matsumura and Nakamori, 2004). Because nickel (Ni) is an economical and active element (Pistonesi *et al.*, 2007, Oliveira *et al.*, 2009, Oliveira *et al.*, 2010, Xu *et al.*, 2010), Ni catalysts, supported on ceramics, are most common catalysts used industrially for this process. However, these catalysts are also subject to different types of deactivation, such as sintering, oxidation, carbon deposition and sulfur poisoning (Sehested, 2006).

1.3.2 Partial Oxidation of Methane (POM)

In terms of energy efficiency perspective, partial oxidation of natural gas is the most promising among the three processes for syngas production. The H₂/CO

ratio of two produced by this method is also suitable for the synthesis of a variety of value-added chemicals. Partial reforming of methane can be carried out homogeneously or catalytically. The homogeneous methane reforming process for syngas generation has been commercially applied in a GTL plant at Sarawak, Malaysia (Hoek and Kersten, 2004). However, this homogeneous partial oxidation reforming has a number of shortcomings including operation at very high temperature ($>1300\text{ }^{\circ}\text{C}$). Catalytic partial oxidation offers advantage where high methane conversions can be obtained with excellent syngas selectivity at extremely high space velocities (contact time on the order of milliseconds) (Shishido *et al.*, 2009). Despite favorable thermodynamics and fast reaction kinetics, partial oxidation technology has to deal with a number of challenges before it can be widely commercialized. High space velocities coupled with high conversions can cause high local temperatures (hot-spot) on the surface of the catalyst which can result in catalyst deactivation due to sintering or formation of catalytically inactive phases by solid-solid reactions and carbon deposition. Moreover, catalyst deactivation can decrease syngas selectivity and make the process highly exothermic, thereby raising safety concerns.

1.3.3 Carbon Dioxide Reforming of Methane (CDRM)

The major interest in carbon dioxide reforming originates from the demand of the production of liquid hydrocarbons and oxygenates, e.g. acetic acid, formaldehyde, and oxo-alcohols since this reaction gives synthesis gas with a H_2/CO ratio of about one (Bradford and Vannice, 1999). However, this reaction has a disadvantage of serious coking on the reforming catalyst. For this reason, a number of studies have been focused on the development of a coke-resistant catalyst for CDRM (Frontera *et al.*, 2009, García *et al.*, 2009, Liu *et al.*, 2009, Ha *et al.*, 2010). The catalysts based

on noble metals have been found to be less sensitive to carbon deposition (Wu and Chou, 2009). However, considering the high cost and limited availability of noble metals, it is more practical in industrial standpoint to develop group VIII based (non-noble) catalysts with high performance and high resistance to carbon deposition.

Moreover, CDRM process is considered to store solar energy or nuclear energy through a chemical energy transmission system (CETS) (Richardson and Paripatyadar, 1990, Wang *et al.*, 1996). The concept of CETS is shown in Figure 1.2. The endothermic reforming is carried out when energy such as solar energy is available. Then the products can be stored or transported to another location where energy is required. Finally, exothermic reaction is carried out to release energy.

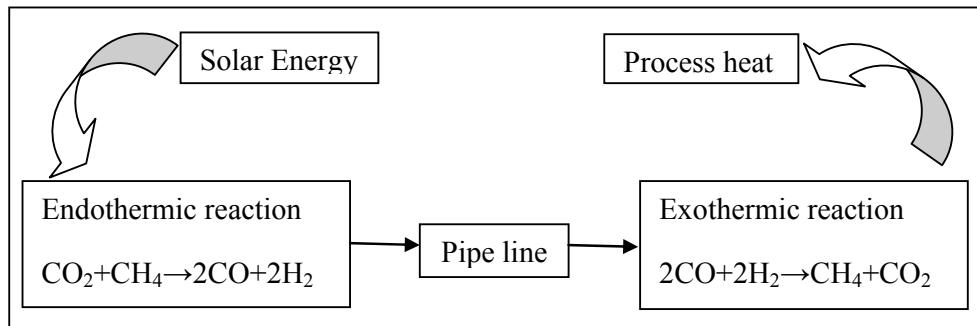


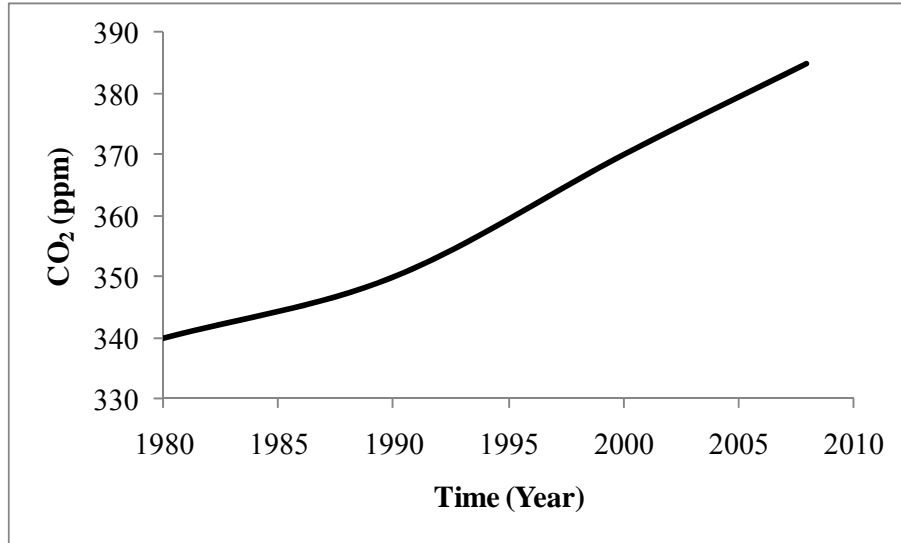
Figure 1.2: The chemical energy transmission system (CETS)(Wang *et al.*, 1996).

From the above brief discussion, it is worth to note that carbon dioxide reforming of methane can be used to mitigate greenhouse gases emission, providing feedstock for liquid hydrocarbon production, or transferring energy via CETS. Carbon dioxide reforming possesses great economic and environmental advantages.

1.4 Greenhouse Effect and Carbon Dioxide Reforming Process

During the past decade, there has been increasing global concern over the rise of carbon dioxide (CO₂) emissions from different sources into the atmosphere that generally accepted as the main contributor for global warming. From the analysis reported by Le Quéré *et al.* (2009), total global emissions of carbon dioxide (CO₂) from the combustion of fossil fuel and changes in land usage (mainly deforestation) in the year 2008 were 27 % higher than in the year 1990. Peters and Hertwich (2008) mentioned in their report that fast growth rates in developing countries (particularly China) in part due to the increased international trade of goods accelerated the growth in fossil fuel CO₂ emissions since year 2000. The future CO₂ levels are expected to rise further due to ongoing burning of fossil fuels. The magnitude of the rise depends on economic, sociological, technological, and natural developments, but may be ultimately limited by the availability of fossil fuels. The carbon dioxide formed in combustion processes is, almost without exception, emitted to the atmosphere where it gradually accumulates (Ross, 2005). Atmospheric CO₂ concentration is more than 105 ppm above its natural preindustrial level when the concentration of CO₂ in the atmosphere reached 385 parts per million (ppm) in 2008 (Figure 1.3a) as reported by Pieter (2009). Through the analysis from Joos and Spahni (2008), CO₂ levels increased at a rate of 1.9 ppm/year between year 2000 and year 2008, compared to 1.5 ppm/yr in the 1990s.

(a)



(b)

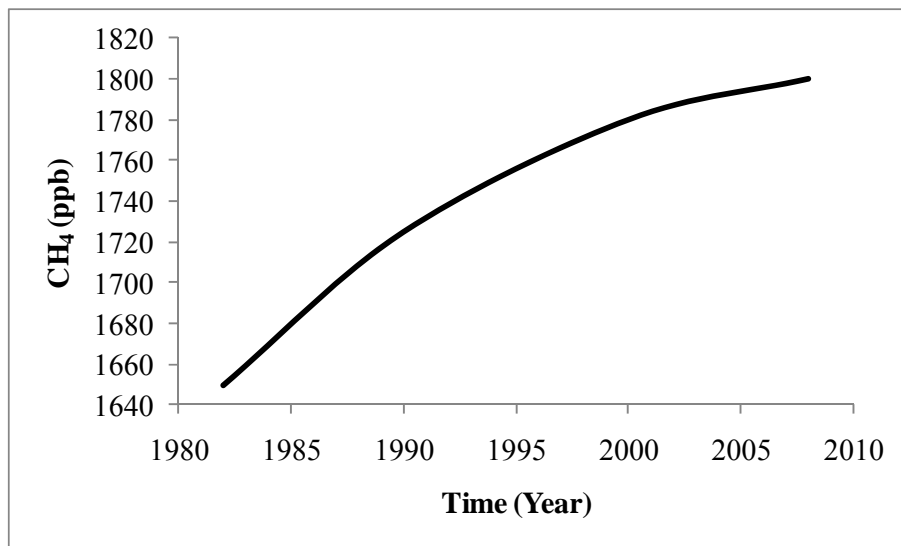


Figure 1.3: Concentration of (a) CO₂ and (b) CH₄ in the atmosphere (Pieter, 2009)

Although the precise CO₂ emission could not be predicted, there are several different indicators which raise the possibility that the greenhouse gases emission will be the main cause of global warming. On the other hand, methane (CH₄) also contributes to the formation of greenhouse gases. The concentration of methane (CH₄) in the atmosphere increased since year 2007 to 1800 parts per billion (ppb) after almost a decade as mentioned in the report by Pieter (2009) (Figure 1.3b).

The causes of the recent increase in CH_4 have not yet been determined but generally CH_4 is emitted by many industrial activities (agriculture activity, biomass burning, mining, and gas and oil industry) and by natural reservoirs (swampland, and peatlands). If the CH_4 concentration further increases for upcoming centuries, it could enhance the greenhouse gas burden of the atmosphere. Consequently, there are many approaches to reduce the concentration of CO_2 and CH_4 in the atmosphere through their utilization. Carbon dioxide reforming/dry reforming of methane (CDRM) is seen as the most potential process to produce value-added liquid fuel through syngas as versatile intermediate.

1.5 Problem Statement

The main concern in catalyst development for CDRM process is always focused on the inhibition of coke deposition on the surface of catalyst. Although many efforts have been reported, the soot formation that causes the deactivation still remains as the most severe drawback. Consequently, catalyst deactivation from coke deposition preventing CDRM process needs to be explored. The present work is to develop a stable Ni-based bimetallic catalyst that, for which it exhibits superior performance for CDRM process compared to Ni-monometallic catalyst.

Fundamental knowledge concerning the coking process is required to improve the coking resistance of a nickel-based catalyst for CO_2 reforming of CH_4 to a degree acceptable for industrial application. These include studies on carbon deposition and its influence on the stability of the catalyst, effect of metal–support interactions on the kind of deposited carbon and its reactivity, individual role of CH_4 and CO_2 reaction pathways in the accumulation of adsorbed carbon under reforming

reaction conditions, chemical and morphological properties of the carbon species formed as well as the kinetics of the reforming reaction.

CDRM using CO₂ needs suitable non-noble catalyst for this process to be utilized in the production of syngas. Thus, the present research concentrate on the development of suitable catalyst for this process with major focus on the role of this catalyst in the reaction, its deactivation and activity at different process conditions. The kinetic parameters will also be determined by proposing suitable model following the reaction mechanism on the developed catalyst.

1.6 Objectives

- i. To develop different combinations of Ni-based bimetallic catalysts and screen the catalysts based on their catalytic activity.
- ii. To characterize the fresh and used catalysts using different analytical techniques (TPR, TPH, TGA, XRD, TEM, XPS, HRTEM, N₂ Adsorption-Desorption, H₂-chemisorption) to elucidate the physico-chemical properties.
- iii. To study the kinetics of the reforming reaction and estimate the kinetic parameters of the proposed kinetic model based on reaction mechanism.
- iv. To measure the catalytic activity of the bimetallic catalyst at different operating conditions for the carbon dioxide reforming (CDRM) and optimize the operating parameters of the process for the syngas production using Design of Experiments (DOE).

1.7 Scope of Work

The first part of the present study concentrates on catalyst screening which is divided into two series of screening process: first and foremost, active sites screening among different combinations of Ni based bimetallic catalysts. The most potential

catalyst is further investigated in the form of single element (monometallic) and bimetallic. Meanwhile, different characterization techniques are used to study the physico-chemical properties of the catalyst.

The second stage of this study consists of kinetic study, stability study as well as regeneration ability of the used catalyst. Kinetic studies are carried out under differential partial pressure of reactants (45-360 kPa) in a packed bed reactor.

The last part of this research work is process study of the most potential catalyst in a packed bed reactor. Operating parameters investigated include reaction temperature, gas hourly space velocity (GHSV), reactant ratio ($\text{CO}_2:\text{CH}_4$) and oxygen concentration in feed. The responses of the process were measured in the basis of the conversion of the limiting reactant (CH_4), products ratio (syngas ratio), and yield of products. Reaction temperature (700-800 °C), GHSV (8.4×10^3 - 200×10^3 mL/g/h), $\text{CO}_2:\text{CH}_4$ (1-5) and oxygen concentration in feed (3-12 %) on the conversion of methane, syngas ratio, and yield of products are studied using Design of Experiments (DOE) coupled with Response Surface Methodology (RSM). The ranges of these parameters were decided based on literature information and experimental viability of the reaction rig. As carbon deposition can affect the long term performance of the catalyst, the stability and coke combustion behaviour of used catalyst are investigated to gain insights into the relationship between the carbon formation and catalyst deactivation. Regenerability of used catalyst is carried by different combinations of regenerating agents such as air, nitrogen as well as hydrogen.

1.8 Organization of Thesis

The thesis comprises five chapters. Chapter 1 presents the natural gas upgrading technologies either through direct or indirect routes. Besides, a brief review of reforming technologies (steam, carbon dioxide and partial oxidation) for the production of syngas is also given. However, the emphasis is given to the utilization of greenhouse gases in carbon dioxide reforming through catalytic process. The objective of this research work also covered in this chapter as well.

Chapter 2 summarizes the related information published in the literature including the process chemistry, reaction mechanism, catalyst development, catalytic technologies as well as kinetic in carbon dioxide reforming. The latest trend in the scientific investigation in carbon dioxide reforming also covered, starting from the broad study of catalyst materials to the development of latest catalytic technology.

Chapter 3 addresses the preparation methods for the bimetallic catalysts, chemicals involved, as well as the setup of the catalytic packed bed reactor. Besides, this chapter also discusses characterization techniques that are used to analyze fresh, reduced and used catalysts.

Chapter 4 presents the performance of screened catalyst for CDRM reaction in a catalytic packed bed reactor. Extensive studies for the most potential catalyst in terms of characterization as well as long term stability are reported in this chapter. A kinetic model for the reforming process is also given. The process is studied under different operating conditions and statistically analyzed using the Design of Experiment (DOE) and the optimum conditions are predicted using Response

Surface Methodology (RSM) coupled with Central Composite Design (CCD) and presented at the end of the chapter.

The overall outcome obtained in the present study are summarized and concluded in Chapter 5. Suggestion on further improvement of the research work that should be done in the future is highlighted so that further improvement in the research work on the syngas production and the development of more feasible CDRM technology in USM can be achieved.

CHAPTER 2

LITERATURE REVIEW

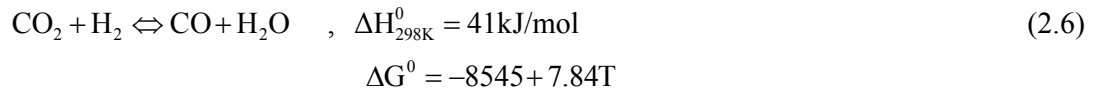
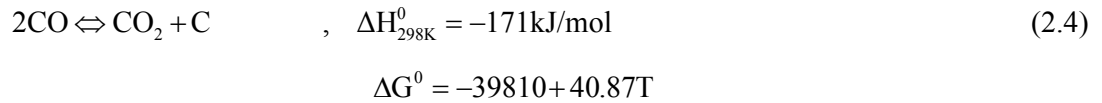
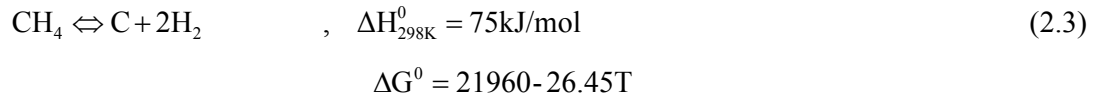
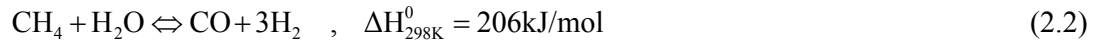
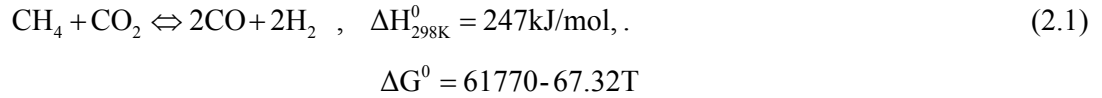
This chapter provides the literature review for this specific research project. Firstly, an overview of carbon dioxide reforming of methane process is discussed in this chapter. Subsequently, literature reports about process chemistry, characterization techniques and reforming mechanism for this reforming process are thoroughly reviewed. Recent development with respect to the catalysts for carbon dioxide reforming including type of active and support materials being use and different preparation method for catalyst are also discussed. Discussion on the kinetics of the reaction is given in the chapter as well. Process study for CDRM reaction is also reviewed for optimization study in the present work and placed at the end of the chapter.

2.1 Overview

The reforming of natural gas with carbon dioxide (i.e. CDRM process) is an attractive reaction for the purpose of both academic study and industrial utilization. There are several advantages for this reaction: (1) mitigation of greenhouse gases (carbon dioxide and methane), (2) transformation of natural gas and carbon dioxide into a valuable syngas, and (3) effective utilization of low grade natural gas resources consisting high concentration of carbon dioxide. Hydrogen in the product could be applied as a fuel in fuel cells (Eriksson *et al.*, 2005, Specchia *et al.*, 2007). The syngas can be converted efficiently to ultra clean fuels with no sulphur and less aromatics such as gasoline, gasoil, methanol, and dimethyl ether (DME) via Fischer-Tropsch synthesis (Choudhary and Choudhary, 2008).

2.2 Process Chemistry

The reaction equilibrium for the production of syngas from CH₄ and CO₂, Equation (2.1) is influenced by the simultaneous reaction of the reverse water-gas shift (RWGS) reaction (Equation (2.6)) which results in H₂/CO ratio of lower than unity.



The standard free energy can be used to calculate the minimum operating temperature for CDRM reaction (Equation (2.1)), methane cracking (Equation (2.3)), Boudouard reaction (Equation (2.4)) and RWGS reaction (Equation (2.6)) and the results are shown in Table 2.1 (Wang *et al.*, 1996).

Table 2.1: Limiting temperature for different reactions of CDRM (Wang *et al.*, 1996)

Temperature (°C)		Reaction
Lower Limit	640	(2.1)
	557	(2.3)
Upper Limit	700	(2.4)
	820	(2.6)

From Table 2.1, it can be concluded that:

- 1) CDRM reaction can proceed above 640 °C accompanied by methane decomposition.
- 2) RWGS reaction as well as Boudouard reaction will not take place when the reaction temperature exceeds 820 °C.
- 3) Formation of carbon is most likely to take place within temperature range from 557 °C -700 °C for both Boudouard reaction and methane decomposition.

Bradford and Vannice (1999) reported that it was thermodynamically feasible for the CDRM reaction when the reaction temperature was higher than 727 °C. Zhang *et al.* (2007) also reported that the CH₄ decomposition (Equation (2.3)) and CO disproportionation (Equation (2.4)) were directly responsible for the carbon deposition on the catalyst. If the reaction temperature was increased from 527 to 627 °C, it showed more preference to carbon deposition than CDRM process. Therefore, the choice of catalyst is very important so that it can kinetically inhibit carbon formation and simultaneously improves the CDRM reaction rate.

Zhang *et al.* (2007) reported variation in the equilibrium constants of the reactions involved as a function of temperature. For a strong endothermic reaction, the equilibrium constant of Equation (2.1) increases dramatically with increasing reaction temperature. Thus, high conversion was favoured at high temperatures. The

equilibrium constants of the moderate endothermic reactions, methane decomposition Equation (2.3) and the reverse water-gas shift reaction (Equation (2.6)), also increased with temperature. Boudouard reaction Equation (2.6) and reverse carbon gasification reaction Equation (2.6), are exothermic and thermodynamically unfavorable at high temperature. Therefore, high reaction temperature (i.e., 750 °C and above) is more favourable to increase the equilibrium conversion of the target reaction (Equation (2.1)) than that of the side reactions (Equation (2.3) to Equation (2.5)). Besides, this process must run with O/C ratios of greater than one to prevent coking of the catalyst.

The propensity of these processes (Equation (2.3) and Equation (2.4)) to form carbon at low O/C ratios is even more pronounced at high pressures. In industry, it would be better to minimize the reactor size and energy use (Shamsi and Johnson, 2003). Tomishige *et al.* (2000) investigated the effect of pressure on CDRM process. Under atmospheric pressure, the catalyst used in the CDRM process was extremely resistant to carbon deposition. Nakamura and Uchijima (1993) concluded that carbon deposition was only possible at 1 atm (atmospheric pressure) when the reaction temperature was increased up to 870 °C. This observation indicated that under atmospheric pressure, the CDRM reaction must be carried out with excessive CO₂ in the feed to avoid carbon formation. Both methane and CO₂ conversions decreased, the H₂/CO ratio decreased while the rate of carbon deposition increased with increasing pressure.

2.3 Characterization Analysis of Common Catalysts

Table 2.2 presents the common characterization techniques that are commonly used to study the catalyst from the perspective of morphology, carbon deposition, type of carbon, changes in phases, active site and support behaviours as well as chemistry of the catalyst itself. It is very important to study the following characterizations of the catalyst used for the CDRM reaction. Table 2.3 presents different types of common characterization technique used for specific type of catalysts.

- Active phases of the catalyst before and after reaction (XRD, TPR, XPS, H₂-Chemisorption and N₂-adsorption).
- Metal dispersion, metal particle size, state of the metal on the supported catalyst (TEM, SEM, XRD, CO-Chemisorption and H₂-Chemisorption).
- Carbon formation and its behaviors (TG, TPO, DTA and TPH).

Table 2.2: Characterization analysis of the catalysts.

Characterization Abbreviation	Analysis	Full Name of the Characterization Analysis
XRD		X-ray Diffraction
TPR		Temperature Programmed Reduction
XPS		X-ray Photoelectron Spectroscopy
EPR		Electron Paramagnetic Resonance
TPO		Temperature Programmed Oxidation
TPH		Temperature Programmed Hydrogenation
TEM		Transmission Electron Microscope
TG		Thermogravimetric
DTA		Differential Thermal Analysis
MS		Mass Spectrometry
TPSR		Temperature Programmed Surface Reaction
AAS		Atomic Absorption Spectroscopy
SEM		Scanning Electron Microscope

Table 2.3: Characterization analysis for CDRM reaction catalysts

Type	Catalyst	Characterization Techniques	Remarks	Ref.
Monometallic Supported Catalysts	Ni/CeO ₂	XRD	Improvement of metal dispersion under plasma treatment.	(Nagaoka <i>et al.</i> , 2003, Ballarini <i>et al.</i> , 2005)
	Pt/Al ₂ O ₃	TPR	Effect of calcination on the reducibility of catalyst.	
	Ni/Al ₂ O ₃	XPS	Surface composition of the fresh, used as well as calcined catalysts.	
	Ni/SiO ₂	EPR	Characterize the structure of support before and after reaction.	
	Ru/SiO ₂	TPO/TPH	To investigate carbonaceous deposit on used catalyst.	
Bimetallic Supported Catalysts	Ni-Co	TEM	Shape of the support and the appearance of the bimetal particles dispersed on the support.	(Kim <i>et al.</i> , 2007, Zhang <i>et al.</i> , 2008a)
	Ni-Ce			
	Ni-Rh	XRD	Crystalline phases of catalyst.	
	Ni-Ru	XPS	Influence of one metal towards another in terms of reducibility.	
		XRF	Chemical composition of the catalyst	
		TG-DTA-MS	Characterization of the deposited coke of used catalyst.	
		TPSR		
		TPO		
		N ₂ -adsorption	Quantitatively measures the surface area and pore size distribution.	
		CO-Chemisorption	Metal dispersion and metal surface chemistry.	
		TPR	Reducibility of catalyst before and after reaction.	

Table 2.3: Continue

Type	Catalyst	Characterization Techniques	Remarks	Ref.
Metal Oxide Supported Catalysts	CoO-MgO CeO ₂	N ₂ -adsorption	To study the decrease of surface area by thermal sintering effect for catalysts calcined at different temperatures.	(Mondal <i>et al.</i> , 2007)
		TPO	Resistance of catalyst towards carbon deposition. (The amount of carbon formed could be calculated from CO and CO ₂ yield TPO profile)	
		XPS	Surface chemical properties of catalyst.	
		XRD	Formation of different crystalline phases under different conditions.	
Promoted Supported Catalysts	Ni-K	TG	Effect of promoters on the gasification of deposited carbon.	(Juan-Juan <i>et al.</i> , 2006, Castro Luna and Iriarte, 2008)
	Ni-Sn	TPH	Reactivity of deposited carbon.	
	Ni-Ca	AAS	Active site and promoters contents before and after reaction.	
	Ni-Mn	TPR	Reduction behavior of catalyst.	
		XRD	Effect of additional promoters on the crystalline structure of the catalyst.	
		TEM	Surface morphology of reduced and used catalyst	
		TPO	Pore size distribution. Amount of carbon deposited	
Perovskites Catalysts	LaNiO _x	N ₂ -adsorption	Effect of calcination temperature on the surface area.	(González <i>et al.</i> , 2005, Lima <i>et al.</i> , 2006, de Lima <i>et al.</i> , 2010)
	LaNiMgO _x	XRD	Information regarding the crystalline structure of the synthesized solid catalyst.	
	LaNiCoO _x	TPR	Temperature programmed reduction condition, changes of phases before and after the reaction could be obtained.	
	LaSrNiO _x	TPR-TPO	Coupling TPR and TPO analysis to study the reversibility of perovskites catalyst (so called redox processes in the reforming reaction).	
	LaCeNiO _x	TEM	Degree of dispersion of active component	

2.4 Mechanism for Reforming of Methane by Carbon Dioxide

It is very important that the mechanism for the CDRM process to be understood and it depends on the choice of catalysts as well as reactants involved in the reaction. The predominant reactive steps between CH₄ and catalyst surface are the dissociation and adsorption, which are claimed to be both direct and precursor mediated (Luntz and Harris, 1991, Seets *et al.*, 1997). However, CH₄ dissociation is gradually shifted from precursor mediated mechanism at low temperature to a direct dissociative at high temperature. Ceyer *et al.*(1988) studied the interaction of CH₄ with nickel (Ni) surface and suggested that in order to dissociate, CH₄ must be separated from its tetrahedral shape to form a trigonal pyramidal structure, after which tunneling of H atom through the activation barrier occurred. However, van Santen and Neurock (1995) claimed that the activation barrier for CH₄ dissociation on Ni did not involve molecular distortion and depended only on the tunneling of H atom via the activation barrier for H abstraction. Nevertheless, neither a quantitative model nor general consensus exists concerning the mechanism for CH₄ adsorption and dissociation on transition metal surface.

On the other hand, it is generally accepted that CO₂ chemisorption and dissociation on transition metal surface is dominated by electron transfer and requires the formation of an anionic CO₂⁻ precursor (Solymosi, 1991). Segner *et al.* (1984) performed scattering experiment related to CO₂ adsorption on Pt and found that CO₂ experienced the equal probability, trapping and desorption i.e. there was no detectable dissociation of CO₂. As a result, there are many attempts to unravel the real CDRM process mechanism that involves both individual activation mechanism for CO₂ and CH₄ reforming. Researchers proposed different mechanisms with respect to their experimental data and observations based on different types of catalyst used

for the reaction. Most of the catalysts reported for CDRM process are made of two components i.e. metallic ones like Ni, Ru, Rh, Pd, Ir, Pt and Co, and oxide supported ones like those of SiO₂, Al₂O₃, MgO, TiO₂, CaO, CeO₂, ZrO₂ and La₂O₃ (Rostrup-Nielsen, 1993). These two components of the catalyst play important roles during the CDRM process.

Generally, methane is only adsorbed on the metal in a dissociated form to produce hydrogen and species CH_x where the value of x is in the range between 0 and 4 and depending on the metal substrate and the reaction temperature. Often, the value of x is around zero to indicate that actually carbon is formed on the metal surface. These species of carbon and hydrogen are attached to the metal active sites. The large majority of the adsorbed hydrogen species are then recombined, producing hydrogen molecules that subsequently desorb in the gaseous phase. It is reported that reversible adsorption of methane on the surface of catalyst leads to cracking of methane and the cracking is a rate limiting step (RDS) while methane adsorption is at equilibrium (Tsipouriari and Verykios, 2001, Topalidis *et al.*, 2007).



where M is the active sites on metals.

Two main categories of support i.e. acidic and basic type supports which account for their distinct behaviour in reaction of each and involve their resistance to carbon deposition based on the observation and data from literature (Ferreira-Aparicio *et al.*, 2000). On the silica supported ruthenium, for example, the dry reforming reaction takes place through a Langmuir–Hinshelwood mechanism. In this case, the dissociative adsorption of CO₂ becomes adsorption limited as the reaction

proceeds due to the accumulation of highly dehydrogenated carbon deposits, which eventually undergo ageing and graphitization on the metal surface. The high concentration of these carbonaceous residues over the metal finally blocks the sites for CO₂ activation, leading to a continuous loss of activity by coke deposition.

On the other hand, a different pathway is proposed for the CDRM reaction over basic type supports such as alumina. CO₂ is activated on the support in the vicinity of the metal particle to form a carbonate species. The carbonate might be reduced by CH_x species to form carbon monoxide (CO). This kind mechanism, in which the support participates in the activation of carbon dioxide, has been proposed by Nakamura *et al.* (1994) for rhodium supported on oxides such as TiO₂, Al₂O₃ or MgO. However, Bitter *et al.* (1997) showed that supports such as ZrO₂ which is neither acidic nor basic exhibited behaviours like basic type support i.e. the CO₂ activation step took place on the support rather than on metal active site. Table 2.4 presents the proposed scheme and reaction steps for CDRM reaction over the metal and support reported in literature. Based on the above discussion and summaries in Table 2.4, a general surface reaction mechanism is proposed to define necessary properties of catalyst for the present research study on CDRM process. As shown in Figure 2.1, the dissociation of methane molecule occurs on the metallic centres as the metallic state of catalyst is believed to be responsible for the CH₄ activation (Wang *et al.*, 1999, Bychkov *et al.*, 2003, Souza *et al.*, 2004, Song *et al.*, 2008).